

A model for luminescence of localized state ensemble

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A distribution function for localized carriers, $f(E, T) = \frac{1}{e^{(E-E_a)/k_B T} + \tau_{tr}/\tau_r}$, is proposed by solving a rate equation, in which, electrical carriers' generation, thermal escape, recapture and radiative recombination are taken into account. Based on this distribution function, a model is developed for luminescence from localized state ensemble with a Gaussian-type density of states. The model reproduces quantitatively all the anomalous temperature behaviors of localized state luminescence. It reduces to the well-known band-tail and luminescence quenching models under certain approximations.

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Carrier localization is a common phenomenon in many material systems such as semiconductor alloys, quantum wells (QWs) and self-assembled quantum dots (QDs). It has profound effects on electrical and optical properties of the materials. It has been known for long that a number of anomalous temperature-dependent luminescence behaviors are related to carrier localization, including 1) the “S-shaped” temperature dependence of the luminescence peak position^{1,2,3,4,5} and 2) a reduction of luminescence linewidth with increasing temperature.^{5,6} Till now, no theory based on microscopic viewpoint is present, which is capable of providing satisfactory explanations for all the anomalous behaviors of the luminescence. In this work, we propose a distribution function for localized carriers and develop a model for the luminescence of localized state ensemble (LSE). The model suggests that thermal redistribution of localized carriers within the localized states is the cause of the anomalies in the temperature dependence of the luminescence peak. It is further shown that the current model reduces to the well-known band-tail model² at high temperature and to the luminescence quenching model of a two-level system⁷ when the distribution of localized states approaches a δ -function. The model is applied to quantitatively interpret the luminescence data of two kinds of material systems, namely InGaAs/GaAs self-assembled QDs and InGaN/GaN QDs. In the former system, LSE naturally form due to size-distributed QDs while in the later, LSE can form due to the In-rich clusters with broad size distribution. The physical implication of $E_a - E_0$ and its effect on the temperature dependence of luminescence peak position are revealed.

For a system with localized electronic states having the density of states (DOS) $\rho(E)$, the rate of change of carriers’ population density $N(E, T)$ in the state at energy E and temperature T is given by⁸

$$\frac{dN(E, T)}{dt} = G(E) + \frac{\gamma_c N'}{\Lambda} \rho(E) - \frac{N(E, T)}{\tau_{tr}} e^{(E-E_a)/k_B T} - \frac{N(E, T)}{\tau_r}, \quad (1)$$

where E_a is the energetic position of a delocalized state to which the localized carriers thermally escape. The first term on the right, $G(E)$, represents the rate of carrier generation, which is proportional to $\rho(E)$ according to $G(E) = \kappa \cdot \rho(E)$,⁸ where κ is a constant proportional to absorption cross section and the number of incident excitation photons. Note that the carrier generation includes both excitation of carriers instantly in localized states and capture of carriers those be excited outside. The second term on the right represents

the number of carriers re-captured by the localized states per unit time, in which γ_c is the recapture coefficient N' is the total number of carriers that are thermally activated away from the localized states as given by

$$N' = \int_{-\infty}^{+\infty} \frac{N(E', T)}{\tau_{tr}} e^{(E' - E_a)/k_B T} dE', \quad (2)$$

in which $1/\tau_{tr}$ is the escape rate of the localized carrier. $\Lambda = \int_{-\infty}^{\infty} \rho(E') dE'$ is the total number of localized states. The third term on the right hand side of Eq. (1) gives the thermal escape rate of the localized carriers and the last term describes the de-population rate of the carriers due to radiative recombination. The term $1/\tau_r$ represents the rate of radiative recombination. τ_{tr} and τ_r are assumed to be the same for all the localized states. In Eq. (1) the tunneling transfer of carriers⁹ between QDs is not taken into account because the non-resonant tunneling rate is negligibly small.¹⁰ More detailed discussion will be given later. The solution of Eq. (1) under steady-state condition ($dN/dt=0$) is

$$N(E, T) = A \cdot n(E, T), \quad (3a)$$

where

$$A = \frac{\kappa \tau_{tr}}{(1 - \gamma_c) + (\tau_{tr}/\tau_r) \gamma_c \xi_1 / \Lambda}, \quad (3b)$$

$$n(E, T) = \frac{\rho(E)}{e^{(E - E_a)/k_B T} + \tau_{tr}/\tau_r}. \quad (3c)$$

In Eq. (3b), $\xi_1 = \int_{-\infty}^{+\infty} n(E', T) dE'$. Further expressing $n(E, T)$ as $n(E, T) = f(E, T) \cdot \rho(E)$, then a distribution function can be derived as

$$f(E, T) = \frac{1}{e^{(E - E_a)/k_B T} + \tau_{tr}/\tau_r}. \quad (4)$$

Note that $n(E, T)$ essentially describes the shape of the luminescence spectrum given by $N(E, T)/\tau_r$, because A is a function of T only. Such a quantity has previously been used to describe the lineshape of phonon-assisted exciton luminescence peaks in some polar semiconductors.^{11,12}

Considering a general case of a LSE system with Gaussian-type DOS, which may result from, *e.g.*, fluctuations of quantum dot size or alloy composition:

$$\rho(E) = \rho_0 e^{-(E - E_0)^2 / 2\sigma^2}, \quad (5)$$

in above, ρ_0 and E_0 are the amplitude and peak energy position, while σ is the standard deviation of the distribution. In Fig. 1, the quantities of $\rho(E)/\rho_0$ and $(\tau_{tr}/\tau_r)f(E, T)$ are plotted with respect to E for both $E_a > E_0$ and $E_a < E_0$. As will be shown in the following, both cases exist in real physical systems as reported in the literature.

As mentioned earlier, $n(E, T)$ represents the “shape” of the luminescence spectrum and the luminescence peak position can be found by setting $\partial n(E, T)/\partial E = 0$. We found that when

$$E = E_0 - x \cdot k_B T, \quad (6)$$

$n(E, T)$ reaches its maximum. The temperature-dependent coefficient $x(T)$ can be obtained by numerically solving the following equation:

$$xe^x = \left[\left(\frac{\sigma}{k_B T} \right)^2 - x \right] \left(\frac{\tau_r}{\tau_{tr}} \right) e^{(E_0 - E_a)/k_B T}, \quad (7)$$

It is not difficult to see that Eq. (7) has one and only one solution for $0 < x < (\sigma/k_B T)^2$.

It should be noted that the temperature dependence described by Eq. (6) is only due to carriers’ thermal redistribution within the localized states. It is known that the bandgap of an idealized semiconductor material without localized electronic states is itself temperature dependent, which is usually described by the Varshni empirical formula.¹³ After taking into account this factor, the variation of the peak position of luminescence from LSE is then given by

$$E(T) = E_0 - \frac{\alpha T^2}{\Theta + T} - x \cdot k_B T, \quad (8)$$

where α is the Varshni parameter and Θ the Debye temperature of the material. For the cases where the thermal redistribution of localized carriers is dominant in the temperature range studied, the temperature dependence of the luminescence peak can be well described with Eq. (6).¹⁴

At high temperature region an approximated solution of Eq. (7) is found to be $(\sigma/k_B T)^2$.¹⁴ Eq. (8) then becomes

$$E(T) = E_0 - \frac{\alpha T^2}{\Theta + T} - \frac{\sigma^2}{k_B T}, \quad (9)$$

which is simply the band-tail model proposed by Eliseev *et al.*² So, the widely adopted band-tail model can be viewed as an approximation of the current model under high T region.

Full width at half maximum height (FWHM) is another parameter for a luminescence spectrum, which is also embedded in $n(E, T)$. The FWHM $\Gamma_c(T)$ of $n(E, T)$ can be obtained by numerically solving $n(E, T) = n(E_{pk}, T)/2$. As will be shown below, the variation of $\Gamma_c(T)$ with temperature exhibits a “valley”, *i.e.*, $\Gamma_c(T)$ decreases first and then increases with raising temperature. Besides the variation in line width due to the thermal redistribution of carriers within LSE, the broadening due to phonon and impurity/imperfection scattering should be taken into consideration. The effective FWHM of luminescence peak is determined by making convolution of $n(E, T)$ and a Lorentzian function, $[4E^2 + (\Gamma_0 + \Gamma_{ph})^2]^{-1}$. Here Γ_0 is due to impurity/imperfection scattering and $\Gamma_{ph} = \sigma_A T + \gamma_{LO}/[e^{\hbar\omega_{LO}/k_B T} - 1]$ due to phonon scattering.¹⁵ In the RRS model¹⁵, σ_A and γ_{LO} are the acoustic- and optical-phonon coupling strength, respectively.

The integrated intensity of the luminescence spectrum is proportional to the total number of localized carriers, *i.e.*,

$$I(T) \propto \int_{-\infty}^{+\infty} N(E', T) dE' = A \int_{-\infty}^{+\infty} n(E', T) dE'. \quad (10)$$

Utilizing an integral approximation:¹⁶

$$\int_{-\infty}^{+\infty} \frac{e^{-x^2}}{1 + e^{a(x+b)}} dx \approx \frac{\sqrt{\pi}}{1 + e^{2.41b \sin \theta}}, \quad (11)$$

where $\theta = \arctan(a/2.41)$, Eq. (10) can be derived as¹⁶

$$I(T) \propto \left\{ 1 + (1 - \gamma_c) \cdot \exp \left[\frac{(E_0 - E_a) + k_B T \cdot \ln(\tau_r/\tau_{tr})}{\sqrt{(k_B T)^2 + 2(\sigma/2.41)^2}} \right] \right\}^{-1}. \quad (12)$$

For $\sigma=0$ (*i.e.*, a δ -functional DOS), the above expression is reduced to the well-known model describing thermal quenching of luminescence for a two-level system.⁷ Indeed, for the case of $\sigma = 0$, no thermal re-distribution takes place and the system becomes essentially an equivalent two-level system. This fact thus further validates the current model, which is more general. Note that for the two-level system, $E_a - E_0$ is in effect the thermal activation energy of the carriers.

Figure 2 shows the calculated profiles for $N(E, T)$ at different temperatures. The parameters used in the calculation are $E_0=1.185$ eV, $E_a=E_0+0.073$ eV, $\sigma=13$ meV, $\tau_{tr}/\tau_r=0.027/250$. From the figure, it is seen that the typical anomalies in the temperature-dependent luminescence are reproduced. Fig. 3(a) plots the peak positions of the spectra as

a function of temperature together with that predicted by Varshni empirical formula using the Varshni parameter $\alpha=0.48$ meV/K and the Debye temperature $\Theta=270$ K. The sum of the two contributions is given by the solid curve, which is seen to agree excellently with the experimental data for an $\text{In}_{0.35}\text{Ga}_{0.65}\text{As}$ QD sample.¹⁷ The QD density of the sample employed in the present work is $\sim 5 \times 10^{10} \text{ cm}^{-2}$. The average distance between QDs is estimated as 20 nm. Other details of the sample have been previously described elsewhere.¹⁸ The non-resonant tunneling rate of carriers between QDs, which is estimated to be $\sim 10^5 \text{ s}^{-1}$ using the Wentzel-Kramers-Brillouin approximation,¹⁹ is not taken into account in the model. It is known that the tunneling rate depends weakly on temperature. However, the thermal escape rate increases exponentially with temperature. For example, at 50 K, the thermal escape rate of carriers occupying QDs with high energy levels (*i.e.*, 58 meV below E_a) reaches to 10^7 s^{-1} . Therefore, the tunneling transfer is disregarded in the model developed for interpretation of temperature-dependence of luminescence of LSE. Figure 3(b) presents the dependence of the FWHM on temperature, from which, it is seen that the reduction of FWHM in the luminescence spectra is mainly due to the effect of redistribution of localized carriers. The effect of phonon scattering is to broaden the spectra monotonously as the temperature increases, whereas carrier thermal re-distribution results in a dependence showing a valley as already mentioned earlier. The combination of the two effect leads to the anomalous dependence of FWHM on temperature shown by the solid curve in Fig. 3(b). In the calculations, the values of $\Gamma_0=5.0$ meV, $\sigma_A=10$ $\mu\text{eV/K}$, $\gamma_{LO}=18.8$ meV and $\hbar\omega_{LO}=36$ meV were adopted.^{15,20} Finally, Figure 3(c) gives the integrated intensity of the luminescence. It can be found that when the recapture coefficient $\gamma_c=0.9$ is taken, the calculated intensity agrees well with the experimental data.

The results presented above is for $E_a - E_0 > 0$. The value of $E_a - E_0$ measures the mean thermal activation energy for the localized carriers. For the system of InGaAs self-assembled QDs investigated in this work, the delocalized state is seen to locate at an energy 73 meV above the central position of the localized states. The origin of such a delocalized state may lie on the presence of a wetting layer due to the S-K growth mode of InGaAs on GaAs.^{5,8}

For the case of $E_a - E_0 < 0$, calculated luminescence peak positions as a function of temperature is given in Fig. 4 for a few selected values of $E_a - E_0$. The other parameters used are also listed in the figure, which remain unchanged for the whole calculations. It is noted that the “S-shaped” temperature dependence of luminescence peaks¹ can be modeled

well. The solid squares stand for the experimental data for an InGa_N/Ga_N QWs.¹⁷ In fact, the experimental data for InGa_N/Ga_N QWs samples reported by other groups^{2,3} can be quantitatively interpreted within the whole temperature range using the current model. Further, for the partially ordered GaInP epilayer system grown on GaAs,⁴ the observed anomalous temperature dependence of the anti-Stokes photoluminescence peak can also be reproduced with the current model.²¹

Finally, we briefly discuss the physical meaning of E_a . Like the Fermi level in the Fermi-Dirac distribution function, E_a in the distribution function derived in the work gives a “marking” level below which all the localized states are occupied by carriers. Its relative position to E_0 essentially determines anomalous temperature dependence of luminescent peak position. For the cases of InGa_N/Ga_N QWs ($E_a < E_0$), E_a may be the quasi-Fermi level of samples,² which depends on concentration of carriers optically/electrically injected and magnitude of the built-in electric field within the samples. It is obvious that the value of $E_a - E_0$ depends individually on sample. As shown in Fig. 4, the magnitude of $E_a - E_0$ determines the details of peak position variation with temperature. Another point we want to mention is that if E_a is far below E_0 , *i.e.*, $E_0 - E_a \geq 8\sigma$, the model will be no longer valid. Under such condition, the luminescent density, $\frac{N(E_a, T)}{\tau_r} \sim 10^{-5}$ (photon number per second), could be too weak to observe when a typical value of $\tau_r=1$ nanosecond was considered.

In conclusion, a model is developed, which quantitatively describes the temperature-dependence of the luminescence spectra from localized carriers. It reproduces almost all the anomalies observed for the luminescence of LSE. It is demonstrated that the two well known band-tail and luminescence quenching models are simply the approximations of the current model under certain limiting conditions.

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Figure Captions

FIG. 1. Normalized distribution function and Gaussian-type density of states for localized carriers. Note that there can be two cases: $E_a - E_0 > 0$ and $E_a - E_0 < 0$.

FIG. 2. Calculated population densities of localized carriers $N(E, T)$, which resemble luminescence spectra, as a function of energy and temperature for the case of $E_a - E_0 > 0$. The curves are shifted along vertical direction for clarity.

FIG. 3. Calculated temperature dependence of luminescence peak position (a); FWHM (b); and integrated intensity (c) for the case of $E_a - E_0 > 0$ using the parameters given for Fig. 2. The squares are experimental data and the solid lines are calculated using corresponding equations as denoted.

FIG. 4. Calculated temperature dependence of luminescence peak position for the cases of $E_a - E_0 < 0$, depicting the “S-shape” dependence curve. The squares are experimental data, the solid lines are calculated by using Eqs. (8) and (7) by setting different values of $E_a - E_0$ as denoted.

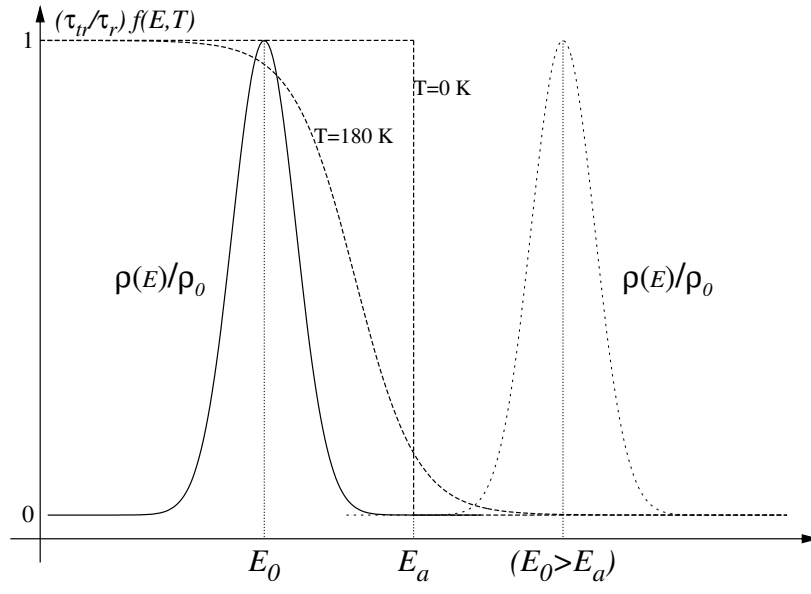


FIG. 1: of 4. Q. Li, *et al.*

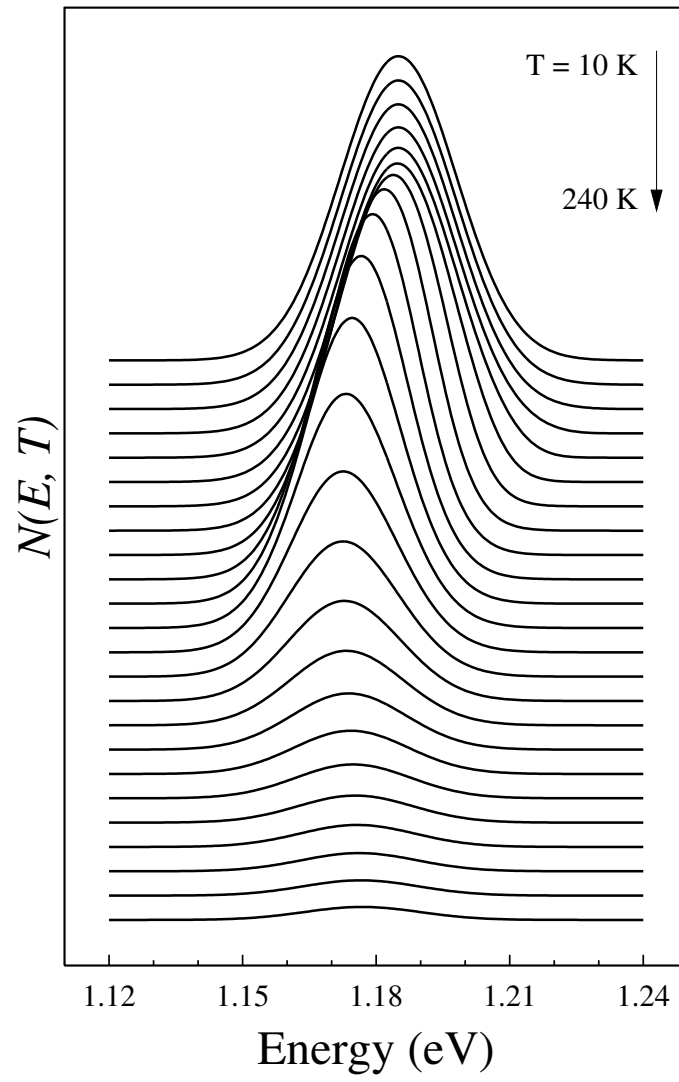


FIG. 2: of 4. Q. Li, *et al.*

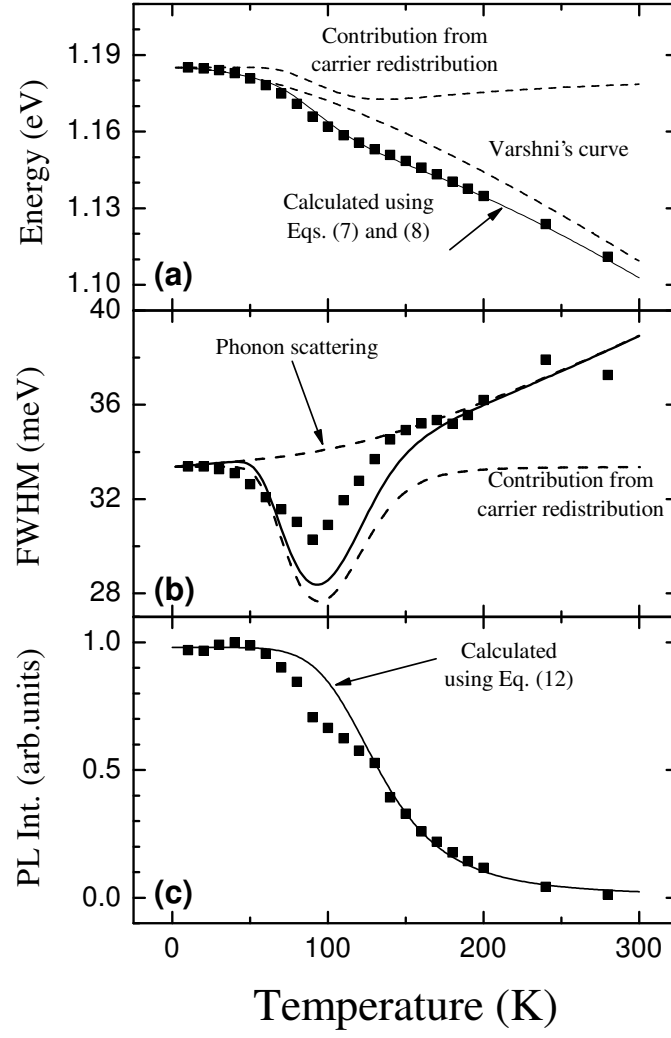


FIG. 3: of 4. Q. Li, *et al.*

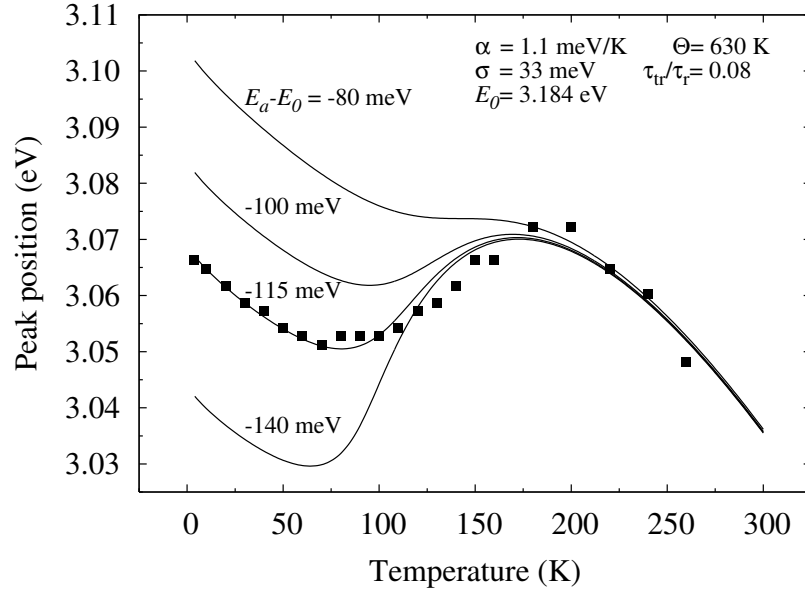


FIG. 4: of 4. Q. Li, *et al.*